Reprinted from ANALYTICAL CHEMISTRY, Vol. 36, Page 888, April 1964

Automatic Osmometer for Determination of Number Average Molecular Weights of Polymers

F. B. ROLFSON and HANS COLL
Shell Development Co., Emeryville, Calif.

▶ An automatic osmometer to determine number average molecular weights of polymers is presented. An operator need only pour in a 10-ml. sample, then isolate it in the cell using the inlet and outlet valves. After a period of about 6 to 9 minutes the osmotic pressure is observed on a Veeder-Root type counter which reads osmotic pressure head in centimeters, tenths, and hundredths. A built-in recorder, the pen of which is directly driven by the balancing servo, enables the operator to follow the servo balancing of osmotic pressure and degree of membrane permeation, if any. The measuring element of the instrument consists of two liquid cavities separated by a semipermeable membrane. The sample cavity includes a thin metal diaphragm which responds to changes in volume. Displacement of this diaphragm from flow of solvent through the membrane is sensed as an electrical capacity change to a fixed electrode in an oscillator circuit, causing a servo to null the solvent head for zero osmotic flow. The performance of the instrument has been studied by determining the molecular weights of eight polymer samples in toluene at 34° C. Results indicate a high degree of precision, and the molecular weights agree well with those from other sources provided no solute can permeate through the membrane.

MEASUREMENT of osmotic pressures in determination of number average molecular weights has not been used extensively in the past because of the time-consuming nature of the classical method and the attendant errors caused by the lengthy observation period. Bruss and Stross (*4*) have discussed some of the dynamic methods described in the recent literature (*7*, *8*, *11*) with some attention to the errors caused by solute permeation of the membrane and the importance of completing the measurement as rapidly as possible. The instrument presented here is the result of an investigation to provide instrumentation to supplement their dynamic method with a view to reducing operator fatigue and possible errors resulting therefrom. A preliminary note describing the essential features of design and operation of the osmometer under discussion has recently been published by one of the authors (*12*).

PRINCIPLE OF OPERATION

As shown in Figure 1, the osmometer cell consists of two cavities separated by a semipermeable membrane. The sample cavity includes a thin metal diaphragm responsive to volume changes and suitable valves to admit a sample, then isolate it. The solvent cavity is connected to a servo-driven plummet in a vertical tube of solvent. The plummet is capable of changing the solvent head, thus causing solvent to flow through the membrane in either direction depending upon the differential pressure. It will be appreciated

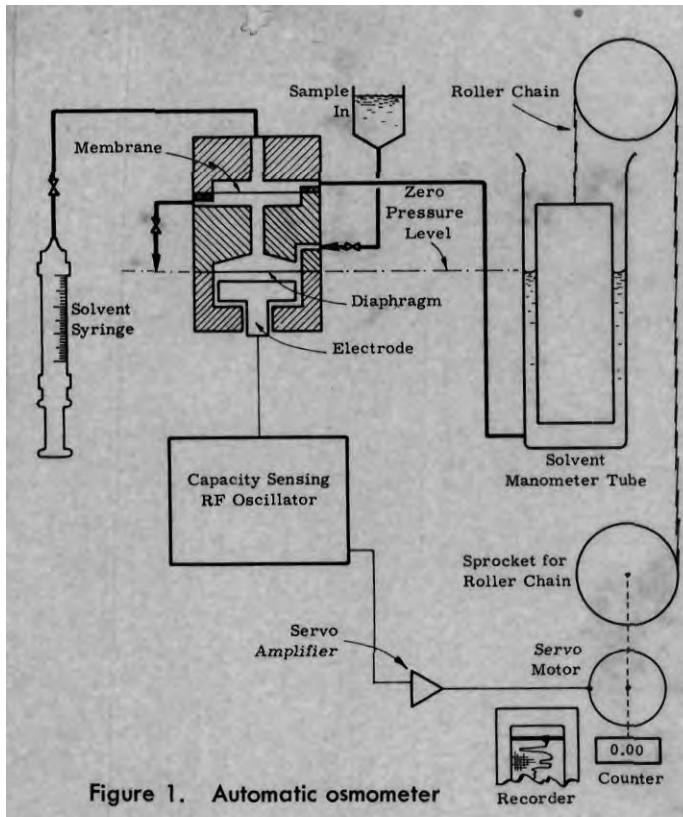

Figure 1. Automatic osmometer

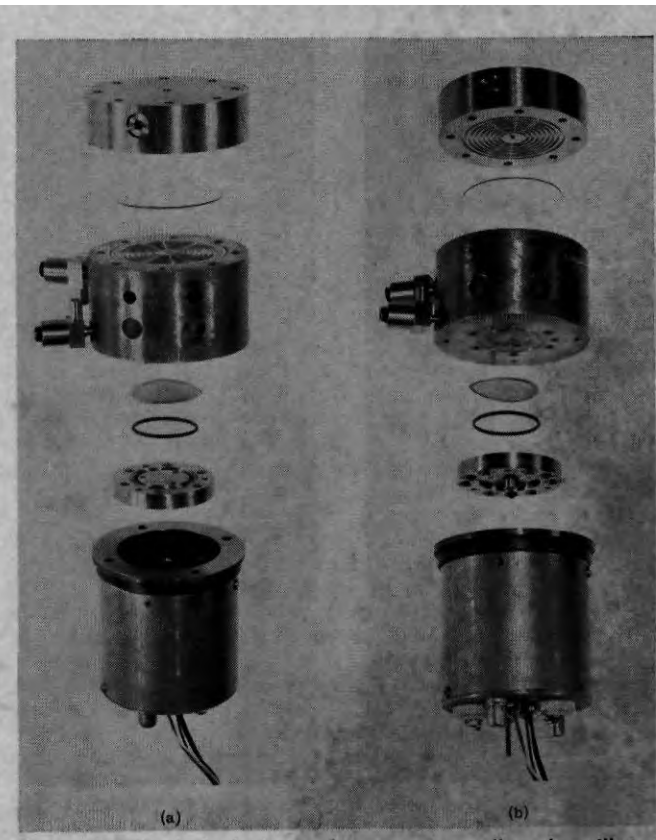

Figure 2. Exploded views of osmometer cell and oscillator

that the metal diaphragm displacement measures the integral of flow; consequently, to satisfy the null position of the diaphragm the volume contained in the sample cavity must be restored to its initial volume at the time the sample was isolated.

Displacement of the metal diaphragm causes a change of capacity to a fixed external electrode which actuates the servo, via the capacity sensing oscillator and amplifier, to restore the null condition including zero osmotic flow.

The witness line (Figure 1) marked "zero pressure level" depicts the relative elevation of the diaphragm, the lower extremity of the outlet drain, and the solvent manometer liquid level at null for zero osmotic pressure. This situation is initially obtained by adjusting the trimmer capacitors of the capacity sensing oscillator with the sample cavity empty. Under this condition the diaphragm has zero (atmospheric) pressure on both sides. When a polymer sample is admitted to the cell, the outlet valve is closed after first having closed the inlet valve, thus establishing an initial pressure of zero at the elevation of the diaphragm because of the elevation at which the sample drain line is terminated. Temperature effects will be discussed later. Solvent immediately commences to flow through the membrane into the polymer sample increasing its volume which deflects the diaphragm causing the servo to raise the manometer plummet thus reducing the solvent pressure on the top side of the membrane as the meniscus falls below the zero level. At null balance the servo comes to rest with the solvent meniscus depressed by the amount of the osmotic pressure. The mechanical counter geared to the plummet servo will now register this depression and hence the osmotic pressure in centimeters, tenths, and hundredths. The recorder will show the entire balancing cycle and by the slope of the curve following the maximum indicated osmotic pressure, the degree of solute permeation through the membrane.

The solvent syringe and valve are used in initially filling the solvent cavity and subsequently to replace solvent which may have been contaminated by smaller polymer molecules which have passed through the membrane.

DESIGN CONSIDERATIONS

Volume of the Cell. A small volume cell is desirable to accommodate small samples, but of greater importance is the effect of cell volume on sensitivity to temperature variations. In this instrument osmotic flow is measured by the resulting change in the volume of a confined sample. Unfortunately, temperature changes also produce changes in volume which are indistinguishable from those resulting from osmotic flow. This is equally true of any detecting system which measures volume, and the effect is proportional to the sample volume. On the other hand, the cell volume should not be minimized as this would magnify side effect errors such as dilution of the sample by the solvent. Then also, practical considerations such as sample flushing, filling, and bubble entrapment dictate a cell volume which is large compared to that resulting from osmotic flow. The volume of the cell presently in use is about 1.5 ml. total from inlet valve to outlet valve.

Volume Measuring Diaphragm. The measuring system must be responsive to small volume changes and the diaphragm sufficiently responsive to pressure changes to provide a stable base line or zero pressure reference of the desired accuracy of 0.01 cm. of solvent head. The small volume requirement has been met by providing a system capable of operating the servo on diaphragm deflections of 2.5×10^{-8} cm. produced by a volume change of less than 0.001 μl. Diaphragm deflection is detected as an electrical capacity change to a fixed electrode in an *r-f* oscillator circuit. The *r-f* oscillator servo amplifier system is nominally tuned so the servo motor is stopped or nulled when the diaphragm is exposed to equal (atmospheric) pressures on both sides and is, therefore, not deflected. Because of residual drift in the oscillator or amplifier, the motor may commence to run, requiring some deflection of the diaphragm to restore the null condition of no rotation. By making the diaphragm sufficiently responsive to small pressure changes, the required deflection will result from a pressure differential of no more than 0.01 cm. of solvent, the stability sought. The capacity sensing oscillator is adjusted to have a sensitivity of 1-volt output for a capacity change of 0.05 pf. The servosystem responds to 0.01 volt at the amplifier input equivalent to a diaphragm capacity change of 5×10^{-4} pf. With simplifying approximations, the analysis of Lilley (*10*) would indicate a displacement of 7.9×10^{-8} cm. with a volume swept out of 0.48×10^{-9} liter for the assumed capacity change of 5×10^{-4} pf.

Typical pressure sensitivity of the diaphragm is 1-cm. solvent head for 0.5-pf. capacity change.

Semipermeable Membrane Support. In a system responsive to small volume changes it is quite apparent that the membrane must be supported in a stable manner, and yet expose a considerable portion of its area to the sample on one side, the solvent on the other. At first glance, it might seem desirable to maintain the membrane in a fixed position, but considerations of the dimensions and requirements involved would indicate the futility of any such wish. Fortunately the movement of the membrane upon application of pressure is not only tolerable but highly desirable, as will be seen from the following considerations. Assume a fixed membrane. Without becoming involved in feedback theory, it is apparent that any change of solvent pressure (produced by servo action) would only very slowly be "seen" by the detecting diaphragm, due to the slowness of osmotic flow. A simple servo would be hopelessly unstable as it would repeatedly overshoot and never come to rest.

Consider a membrane that deflects upon application of pressure. Any change in solvent pressure produced by the servo will now be transmitted to the diaphragm and the simple servo will be inherently stable. The membrane, having been deflected by the solvent pressure, must now relax to its null position as osmotic flow proceeds.

The manner of supporting the membrane can be seen in the exploded view of the cell, Figure 2.

Temperature Effect. The osmotic pressure itself varies directly with the absolute temperature so that one could simply read a thermometer inserted in the cell and make a suitable correction of the required accuracy without much difficulty. More important is the change of volume produced by any temperature change. Specifically this temperature-volume change must be made small compared to that produced by osmotic flow as the pressure differential approaches zero (say, 0.01-cm. head). Accordingly, the rate of change of temperature must be held to about 0.001° C. per minute. In the absence of good temperature control, a steady or nonvarying readout on the instrument does not necessarily imply that a constant temperature prevails. It may just as well mean that a constant temperature drift exists whereupon the constant reading will be in error by the pressure differential required to produce an osmotic flow which just offsets the volume change due to the temperature drift.

In addition to the foregoing basic physical considerations, the matter of mechanical stability of the diaphragm, sensing electrode, and associated *r-f* oscillator circuitry is of prime importance. For this reason the oscillator has been mechanically and thermally associated with the temperature-controlled osmometer cell. Although the measuring circuit has been designed to have good temperature stability, the added nsurance provided by the constant temperature environment is more than welcome.

The metal for the cell body needs to have high thermal conductivity to keep the thermal response time within reason. Cells of both copper and aluminum have been used satisfactorily.

Sample Valves. The sample valves must be leak-tight in view of the small osmotic flow. They should be thermally close-coupled to the cell and small enough so as not to present an unduly large heat sink because sample in the valves is equivalent to sample in the cell so far as low-volume and constant - temperature requirements are concerned.

At least one of the two valves (outlet) must not change volume on closure. Were it to do so, valving off the sample would add an initial pressure to be overcome by osmotic flow. Excessive pressures on the membrane are to be avoided to minimize hysteresis effects. The sample outlet or drain line is arranged to be open to the atmosphere at the diaphragm elevation. This permits the establishment of an initial pressure of zero by closing first the inlet valve, then the outlet valve.

DESCRIPTION

General. The instrument is housed in a single cabinet, 12 inches wide, 15 inches high by 13 inches deep, the weight being about 50 lb. It is supported on five equal shock mounts, one at each corner plus one additional mount located so as to equalize the load on all the mounts in the presence of an off-axis center of gravity. Figure 3 shows the general arrangement. The cabinet houses the line voltage regulator, the servodrive, servoamplifier, thermoregulator, and a double wall chamber for thermal isolation enclosing the osmometer cell. For low-temperature operation (a few degrees above the ambient) a small induced-draft exhaust fan draws a low-velocity air flow upward between the two walls of the cell enclosure to provide a heat sink for the thermoregulator to work against. The same fan also ventilates the other portions of the main cabinet to maintain a reasonably low temperature throughout the entire instrument.

Operation at a cell temperature of 135° C. has been accomplished with only minor changes. The spaces between the double walls are filled with thermal insulation, two cartridge heaters are added to the walls of the inner enclosure, and the cartridge heaters in the cell itself are changed. The thermoregulator supplies a total of 25 watts to all heaters at 135° C. For fast warmup, a relay parallels all heaters and connects them to the power line to provide 200 watts. When the desired temperature is reached, the relay drops out and returns the heaters to the regulator. The sample funnel is replaced with a small cavity thermostated at about 140° C. to preheat the sample and hold the solute in solution.

The capacity-measuring *r-f* oscillator is fastened directly to the cell and consequently shares the same enclosure. The necessary solvent lines, electrical conductors, and sample drain penetrate the double wall enclosure via three hollow nylon standoffs which also serve as nonconducting supports under the inner chamber. An open compartment at the lower left (Figure 3), provides space for a small beaker, directly under the cell, to catch the outgoing sample. Access to the oscillator-tuning capacitors is available through this compartment.

Another penetration out the top side of the enclosure consists of a $1^1/_4$ inch in diameter thin-walled Bakelite tube, which terminates at the top of the instrument, and provides an entrance for the sample funnel.

The two small valves located on the front panel, marked "Solvent Inlet" and "Solvent Outlet" are borrowed from the medical profession. They provide a convenient means for manipulating the solvent using hypodermic syringes. These handy fittings are used throughout the solvent circuit but they are not adequate for use in the sample cell.

Sample Cell. The schematic diagram, Figure 1, along with the exploded view of Figure 2 will clarify the sample flow scheme. The concentric ring configuration which combines effective membrane support with relatively high surface area exposure is identical to the design of Bruss and Stross (*4*), only the flow pattern has been altered to assure complete flushing and prevent bubble entrapment in the present horizontal disposition of the membrane. With both valves opened, the sample enters the cavity above the diaphragm at a point near its circumference. The passageways here are small enough ($^1/_{16}$ inch in diameter) to be swept clear of bubbles. The cavity above the diaphragm has a conical top which effectively causes bubbles to pass upward through the axial passageway leading to the membrane support. The passageway consists of alternate concentric grooves and lands each $^1/_{16}$ inch in width. A milled groove connects the axial hole with the inner concentric groove. From here the flow divides into two parallel paths formed by the two halves of the circle. Diametrically opposite where the sample entered the innermost circular groove, the surrounding land is cut through, permitting the flow to enter the second concentric groove where it again divides and so on until all the grooves have been traversed, the outer one then discharging to the outlet valve and out the drain. Thus each concentric groove forms two equal parallel paths which are in series with the parallel paths of every other groove. The outermost groove in the cell block receives a Teflon O ring for a liquid seal.

Solvent Cell. The membrane support in the solvent cell is similar to that in the sample cell. The main difference is in the omission of the O ring groove and the addition of an outer groove, whose function is to keep the edge of the membrane in contact with the solvent.

The solvent inlet at the top center is

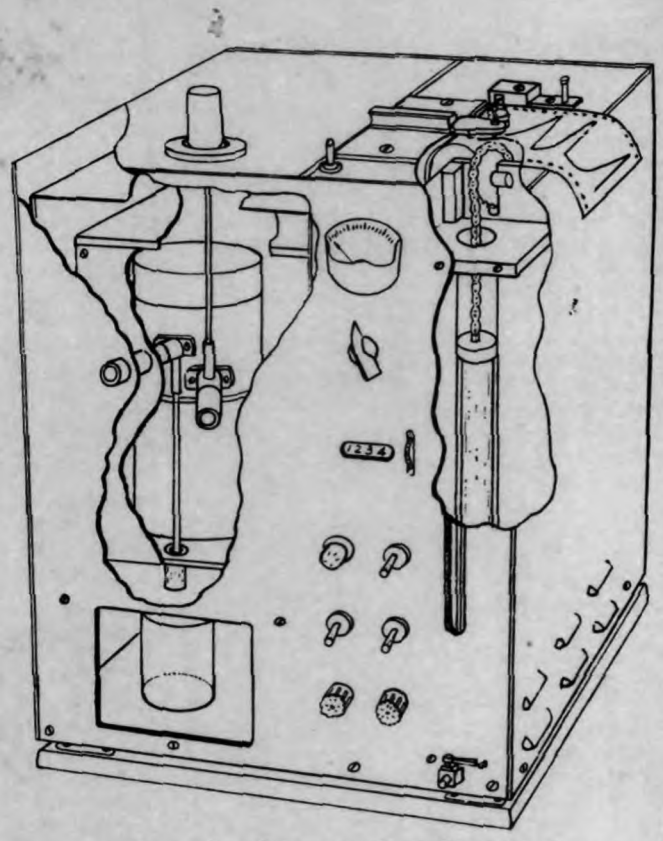

Figure 3. Cut-away view of instrument

Cell mounting in its inner and outer enclosure and arrangement of sample inlet and drain tubes as well as other features described in text

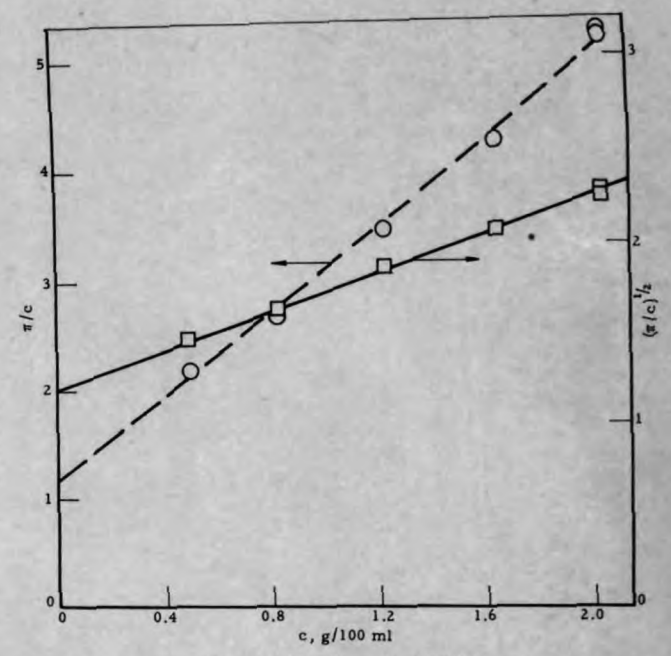

Figure 4. Sample S 111

Plot of reduced osmotic pressure, π/c, and $(\pi/c)^{1/2}$, vs. concentration. Dashed line shows a linear extrapolation which results in a lower intercept $(\pi/c)_0 = 1.20$ compared with 1.44 from the square-root extrapolation. Pressure in cm. toluene, concentration in g./100 ml.

piped to the valve on the front panel. Fresh solvent, uncontaminated by small solute molecules which may have permeated the membrane, can be added at this solvent inlet valve. When this is done, a like amount is withdrawn from the sample outlet valve on the front panel which connects with the bottom of the manometer tube. The other solvent port is piped down through one of the nylon standoffs, hence to the lower end of the manometer tube.

Valves. Special valves of the self-centering floating-ball type were designed for the sample side of the sensing cell. They have the small volume essential for minimum extraneous cell capacity and for close thermal coupling to the cell. They also meet the requirements of being leak-tight and of not changing volume on closure, both necessary on the hydrostatically confined sample volume. They are provided with removable simple torque wrenches which provide uniform closure. By being removable, the wrenches do not contribute to the heat loss of the cell thus relieving some burden on the thermoregulator.

Diaphragm. The diaphragm is 0.0015-inch thick beryllium copper. It is stretched as indicated in the exploded view, Figure 2, by an O ring and suitably grooved retaining ring. The liquid seal for the sample cell is metal-to-metal with the O ring providing the required pressure.

Capacity Electrode. Mechanical stability of the capacity electrode system is highly important. Electrode spacing must be held constant within a fraction of a microinch commensurate with typical diaphragm displacement of only 0.4 microinch. The required stability is attained by spacing the fixed electrode from the diaphragm a distance of 0.00183 inch with 0.120-inch diameter synthetic ruby watch jewels. The thinness of the jewels provides a support length subject to thermal expansion of approximately the 0.00183-inch spacing. The small area of the jewels minimizes the effect of their temperature coefficient of dielectric constant. The electrical capacity of the cell is adjusted to 100 pf., ±3% by diamond lapping the jewels.

Capacity Sensing Oscillator. A crystal controlled radio frequency oscillator used somewhat in the manner described by Henriquez and Renaud (*9*) and later by Alexander (*1*), has been further developed to provide a smooth transition between the oscillating and nonoscillating regions where the rise in cathode current is extremely sharp. To provide a reversible direct-current output, the positive voltage produced across the cathode resistor is compared to a constant positive voltage which is equal to the cathode voltage for the cathode current selected as the null capacity point.

Excellent temperature stability of the anode circuit has been obtained by use of a self-compensating inductor fashioned on the principles described by Seeley and Anderson (*13*), trimmer capacitors of the piston type having quartz dielectric and invar pistons (J.F.D. Co., Brooklyn, N. Y.), and an RCA 6CW4 Nuvistor triode as the oscillator tube.

Servoamplifier and Motor. The servoamplifier is direct coupled, using two pentodes as a long tailed pair for voltage amplification and phase inversion, followed by a pair of power pentodes which serve predominantly to load one or the other of the two wound shading coils of the Barber-Colman (Rockford, Ill.) motor to produce a rotation, whose direction depends on the polarity and magnitude of the input signal from the oscillator and reference voltage. A signal of about 10 mv. is required to reverse the motor, and zero stability, after brief warmup, is of the same order.

Servosystem and Recorder. The Barber-Colman servomotor is supplied with a 236:1 gear reduction. To this unit an additional 3:1 reduction is added to drive a miniature chain sprocket, whose rotation is restricted to somewhat less than a complete revolution by mechanical stops. One end of the chain is fixed to the sprocket while the free end wraps around, then is led upward over a second sprocket, then down to the metal plummet in the solvent manometer tube, so that servoaction raises and lowers the plummet changing the solvent height as it does so. The second sprocket is fitted with a dial cable and pulley which actuates the pen on the strip chart recorder. The weight of the metal plummet effectively loads out any backlash in the servogearing, thus producing a high resolution system with complete absence of backlash in the recorder as well as the servo proper.

The combination of a cylindrical metal plummet immersed in a precision-bore manometer tube permits complete freedom in the choice of scale factors

and provides assurance of any usable degree of precision and linearity. The opportunity for deliberate nonlinearity also exists. For example, by machining large size ends on the otherwise cylindrical plummet, large changes in a liquid height could be produced at either end of the travel to enhance recovery from saturation. This has not been done as yet because the fast membranes used so far have not required it.

Thermoregulator. The electronic thermoregulator employs a resistance thermometer in a balanced bridge circuit, which is transformer-coupled to a three-stage high-gain amplifier terminating in a cathode-coupled phase inverter. The phase inverter stage controls a pair of small thyratrons, which furnish the current for maintaining the cell temperature constant. The bridge circuit, as well as the thyratron anodes, is operated at line frequency through a special transformer having a well shielded bridge supply winding to eliminate spurious quadrature phase voltage, which would otherwise be present in the low level bridge output at balance. Proportional control of the thyratrons is obtained by the conventional method of superimposing a constant quadrature component of grid bias on the in-phase amplifier error signal from the bridge. The quadrature component is conveniently obtained from the filament supply through a low pass *RC* pair connected to the normally grounded grid of the cathode coupled phase inverter.

MOLECULAR WEIGHT DETERMINATIONS

The performance of the automatic osmometer described in the preceding sections was studied by determining the molecular weights of a series of poly-*a*-methylstyrene (PAMS) and polystyrene samples in toluene at 34° C. All samples except one, Dow Styron 666, represented polymer which had been fractionated to minimize the spread of molecular weights so that the weight-average molecular weight from light scattering may also serve as a guide for evaluating the accuracy of the osmometric results.

Materials. The samples designated as PAMS 1 to 4, and PAMS 025 are poly-*a*-methylstyrenes prepared and fractionated as described by Burge and Bruss (*5*). PAMS 1 to 4 are identical with their samples No. 1, 3, 5, 7. S102 and S111 represent International Standard Polystyrenes (*2*) (obtained by courtesy of J. V. Stabin, Brooklyn). Dow Styron 666 is commercially available polystyrene, which for some of our measurements had been precipitated from toluene by means of an excess of methanol. Reagent grade toluene (Baker and Adamson) was used without further purification, however, with the precaution that for all measurements solvent and sample chamber were filled with toluene from the same batch to avoid transient osmotic pressures from impurities in the solvent (*6*). Gel cellophane membranes No. 600 (J. V. Stabin, Brooklyn) were used throughout this work. The membrane in the automatic osmometer has been in use for 10 months.

Generally the following procedure was found useful for the molecular weight determinations: sample and solvent chamber were flushed with portions of solvent, and two to three blank curves recorded over a period of about 15 minutes each (pure solvent on both sides of the membrane) to assure reproducibility of the base line. An agreement of blank values within ±0.02 cm. solvent head was considered satisfactory. Next, a polymer solution of a concentration to give osmotic pressures above 5 cm. was introduced, and the osmotic pressure–time curve was observed for at least 30 minutes. This preliminary experiment indicated the useful concentration range for the determination on hand; its main purpose, however, was to establish whether solute components small enough to pass through the membrane were absent, as witnessed by constancy of osmotic pressure. Next, the sample chamber was flushed and one more blank curve recorded. Agreement with the previous blank curves as to shape and final value is an additional indication for the absence of permeating solute. Once this had been established the usual procedure was to measure the osmotic pressure of the most dilute solution (less than one third of the highest concentration) in duplicate, followed by samples in an ascending concentration sequence, the minimum being five experimental points without intervening blanks. The volume of each solution amounted to 8 to 10 ml. of which all except the last portion of about 2 ml. was used to flush out the previous sample. Osmotic pressures observed after 15 to 30 minutes were used for the calculation of the molecular weight. Reduced osmotic pressures, π/c, or their square roots, $(\pi/c)^{1/2}$, were plotted against concentration and graphically extrapolated to infinite dilution. For the conditions under consideration the number-average molecular weight, M_n, is calculated as

$$\bar{M}_n = \frac{RT}{(\pi/c)_0} = \frac{3.02 \times 10^5}{(\pi/c)_0} \qquad (1)$$

$(\pi/c)_0$ designates the reduced osmotic pressure at infinite dilution. π is in cm. of toluene, T = 307° K., and c is concentration in grams/100 ml. The density of toluene refers to 27° C., the temperature of the manometer. It was observed that an osmotic pressure measurement on a solution of a given concentration gave somewhat low values if preceded by a blank instead of a solution of the same concentration, probably due to a dilution by the solvent retained by the membrane. A sequence of readings, such as blank, π, $\pi + 3\%$, $\pi + 4\%$, and $\pi + 4\%$, was found typical. In accordance with this observation and the scheme of measurements outlined above, the experimental molecular weights were corrected by subtracting 2%. If solute permeation was indicated, sample and solvent chamber were flushed and a blank measurement was taken before each new polymer solution was introduced. In this latter case, the osmotic pressures were extrapolated back to zero time and a correction of −4% applied to the molecular weights to take care of the error introduced if a polymer solution is preceded by a blank.

Since toluene is a good solvent for the polymers under consideration contributions from the third virial coefficient, Γ_3, should not be ignored, particularly not in the case of samples of high molecular weight (*16*). Thus,

$$\left(\frac{\pi}{c}\right) = \left(\frac{\pi}{c}\right)_0 [1 + \Gamma_2 c + \Gamma_3 c^2] \qquad (2)$$

The value of Γ_3 being unknown, we assume $\Gamma_3 = 0.25\ \Gamma_2^2$, which appears to be a better approximation than ignoring the quadratic term. Equation 2 can then be written as

$$\left(\frac{\pi}{c}\right)^{1/2} = \left(\frac{\pi}{c}\right)_0^{1/2} \left[1 + \frac{\Gamma_2}{2} c\right]$$

and one obtains a linear plot for $(\pi/c)^{1/2}$ *vs.* concentration. Such an approach is somewhat arbitrary, but the limited number of experimental points and the error associated with each measurement in general do not allow a meaningful evaluation of Γ_3. Only in the case of PAMS 1, 2, and 3 we have applied a "linear" ($\Gamma_3 = 0$) instead of a "square-root" extrapolation; here Γ_2 is sufficiently small, and the concentrations are low enough to assure practically the same intercept for either method of extrapolation. Furthermore, an analysis of the data for PAMS 3 showed that an equation which includes $\Gamma_3 c^2$ does not give a better fit (Γ_3 arbitrary). We note that for a given set of points, square-root extrapolation will generally lead to a lower molecular weight than linear extrapolation (Γ_2 and $\Gamma_3 > 0$), the discrepancy becoming more pronounced with increasing molecular weight. Figure 4 shows a plot of either kind for sample S 111.

One polymer, PAMS 3, was subjected to 19 measurements in a random manner. The concentration range extended from 0.15 to 0.7 gram/100 ml. solution. No correction of the individual points for the previously mentioned dilution effect was applied, because of the difficulty of estimating the exact magnitude of such a correction for each point. The resulting molecular weight is therefore probably too high by 1 or 2%. Fitting the function $\pi = ac + bc^2$ to the experimental points by the method of least squares gave a molecular weight of 23,300 with a relative standard deviation of ±1.1%.

Of special interest are the osmotic-pressure curves obtained with Dow Styron 666. Figure 5 shows a superposition of such curves at a concentration of 1.15 grams/100 ml. Extensive solute permeation was exhibited by the unprecipitated polymer (*A*); single precipitation removed some of the low-molecular weight component (*B*), while reprecipitation of the once precipitated material apparently removed all of the permeating species (*C*). This be-

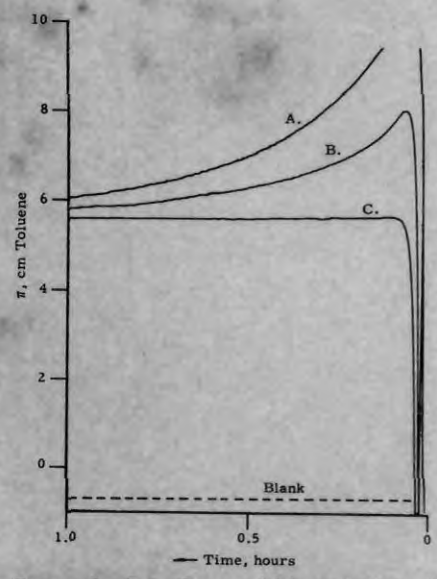

Figure 5. Dow Styron 666, variation of osmotic pressure with time

A: Unprecipitated polymer
B: Polymer precipitated once from toluene with excess of methanol
C: Polymer precipitated twice
Concentration: 1.18 g./100 ml. Pressure in cm toluene.

havior can be explained by the presence of a few per cent of low-molecular-weight plasticizer, which is removed by successive precipitation. From curve *C*, Figure 5, it can be seen that the equilibrium pressure is attained within a few minutes.

For comparison we determined the molecular weight of some of the samples by means of a manual small-volume osmometer (*3*), equipped with 2 gel cellophane membranes No. 600, and a reading capillary of 0.2-mm. i.d. Because of the small capillary diameter, static pressure readings could be taken within 30 minutes after filling of the osmometer. By comparison with the automatic osmometer, corresponding pressures determined manually appeared to be consistently somewhat lower and more erratic. Table I summarizes the results.

DISCUSSION

PAMS 1 and PAMS 2. Solute permeation was clearly indicated by the decline of osmotic pressure with time (Figure 6) in which case even the extrapolated pressure at time zero, when all of the solute is still on the sample side of the membrane, falls short of the theoretical osmotic pressure (*15*); our present results are therefore too high. Burge and Bruss (*5*) in their work used a very slow but highly retentive membrane (Schleicher and Schuell, Superdense).

PAMS 3. Solute permeation was not detectable, yet we found a molecular weight which differed from that of the other authors (*5*) by more than 10%, while the standard error of the molecular weight calculated from 19 experimental points amounted to only 1.1%. Despite the apparent good agreement of dynamic and static results by Burge and Bruss, those authors consider it possible that their result is in error by 10% (private communication). Likewise, results from our manual measurements (4 points), although of not very high precision, are incompatible with a molecular weight below 23,000.

PAMS 4. The agreement between results is satisfactory.

PAMS 025. The agreement of results from automatic and manual measurements is good. Linear extrapolation would raise either result by about 15 to 20%.

S 102 and S 111. The reference values are averages from the results obtained in nine laboratories with toluene as the solvent (*2*); the high and low results in each case were 82,300, 75,000, and 225,000, 196,000, respectively.

Dow Styron 666. Figure 5 shows that in the case of the untreated polymer, initially half of the total osmotic pressure is due to the low-molecular weight species; the apparent molecular weight, here to an even greater extent than for PAMS 1 and 2 (Figure 6), depends on the characteristics of the membrane, and is a "reflection-average molecular weight" (*14, 15*). If the osmotic pressure curve is recorded over a long period of time, information can be obtained whether most of the polymer itself or only a low molecular weight impurity diffused through the membrane. In the latter case a limiting pressure should be reached within a relatively short time because of the higher diffusion rates of small molecules. A comparison of the curves obtained with PAMS 1 and 2, on one hand, and Styron 666, on the other, made this clear: PAMS 1 and 2 showed a more gradual decline and did not reach a limiting osmotic pressure within 10 hours, while unprecipitated Styron 666 had closely approached a limiting value after a little more than 1 hour. From these curves and the low molecular weight of PAMS 1 and 2, we can conclude that a sizable portion of the polymer, if not all of the material can pass through the membrane, while Styron 666 contains an impurity of a molecular weight considerably lower than that of the polymer.

The main advantages of the automatic osmometer are rapid attainment of equilibrium pressure and ease of operation. The useful range of molec-

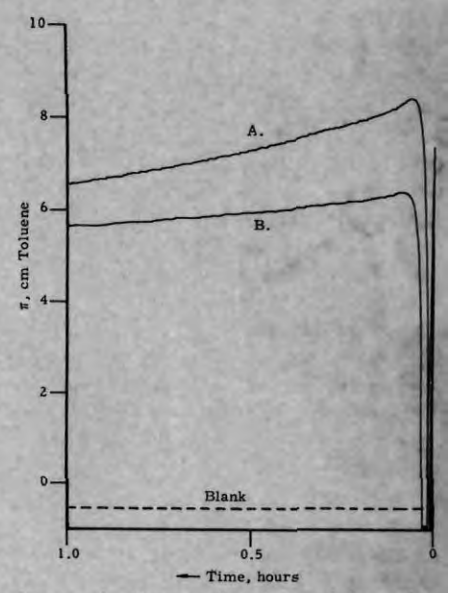

Figure 6. Low-molecular weight poly-α-methylstyrenes. Variation of osmotic pressure with time

A: PAMS 1, 0.0913 g./100 ml.
B: PAMS 2, 0.104 g./100 ml.
Pressures in cm. toluene

Table I. Molecular Weights of Polymer Samples

Polymer	No.-av. mol. wt. × 10^{-3} osmometry: Automatic	No.-av. mol. wt. × 10^{-3} osmometry: Manual	Wt.-av. mol. wt. × 10^{-3} light scattering	Remarks referring to automatic osmometry
PAMS 1	2.87	2.2[a]	3.4[a]	Solute permeation linear extrapolation
PAMS 2	4.30	3.7[a]	5.0[a]	Solute permeation linear extrapolation
PAMS 3	23.3	20[a] (23.5)	25[a]	19 Experimental points linear extrapolation
PAMS 4	58.4	57[a]	64[a]	
PAMS 025	186	(196)	(213)	
S 102	77.5	77.6[b]	90[b]	
S 111	207	210[b]	237[b]	
Styron 666	<50		(295)	Unprecipitated
	98.6	(104)	(295)	Twice precipitated

[a] Burge and Bruss (*5*).
[b] Report by Atlas and Mark (*2*).

Numbers in parentheses refer to results from manual osmometry and light scattering by the authors.

ular weights lies between about 10,000 and 300,000, or higher, depending on how large an experimental error is acceptable. The lower limit, of course, depends exclusively on the retentiveness of the membrane. Extrapolation of osmotic pressure to zero time is greatly facilitated by recording, and thus the error arising from solute permeation can be minimized, although not eliminated. The solvent chamber can easily be flushed which is of importance if solute permeation or membrane asymmetry become noticeable.

The precision of the instrument is equally as good or better than what can be routinely achieved with conventional manual osmometers. The error in the mechanical repeatability of the measurements is not larger than ±0.01 cm., although in practice larger errors may be encountered as a result of imperfect membrane behavior. This became particularly evident at elevated temperatures (135° C.) with decalin as the solvent, under which conditions the stability and lifetime of gel cellophane membranes is greatly impaired. A systematic error or inaccuracy of results is not evident, provided solute permeation does not occur.

Two automatic osmometers operating near room temperature, one at the Shell Chemical Research Laboratories at Torrance, Calif., and the other one in our own laboratory, have been in use for almost 1 year in which they have given highly satisfactory performance.

The automatic osmometer should prove particularly useful for laboratories engaged in polymer research and also in control laboratories of plants engaged in the manufacturing of polymers. License for the manufacture of the instrument has been granted to J. V. Stabin, Brooklyn, N. Y., and also to Hallikainen Instruments, Berkeley, Calif.

ACKNOWLEDGMENT

The authors extend their thanks to W. H. Husing for his mechanical ingenuity in designing the recorder mechanism, to F. H. Stross and D. B. Bruss for helpful discussions on osmometry, and to C. J. Penther for valuable suggestions during the development and assistance in preparation and review of this presentation. The mechanical and electrical skill of J. E. Antczak in the construction of this instrument is gratefully acknowledged.

LITERATURE CITED

(1) Alexander, F. C., *Electronics* **18,** 116 (April, 1945).
(2) Atlas, S. M., Mark, H. F., "Report on Molecular-Weight Measurements of Standard Polystyrene Samples"; Transactions of International Union of Pure and Applied Chemistry, Paris Meeting, 1963 (in print).
(3) Bruss, D. B., Stross, F. H., ANAL. CHEM. **32,** 1456 (1960).
(4) Bruss, D. B., Stross, F. H., *J. Polymer Sci.*, Part A, **1,** 2439 (1963).
(5) Burge, D. E., Bruss, D. B., *J. Polymer Sci.*, Part A, **1,** 1927 (1963).
(6) Coll, H., Stross, F. H., *Ibid.*, Part B, **1,** 641 (1963).
(7) Elias, H. G., *Chem. Ingr.-Techn.* **33,** 359 (1951).
(8) Fuoss, R. M., Mead, D. J., *J. Phys. Chem.* **47,** 59 (1943).
(9) Henriquez, P. C., Renaud, A. W., *Physica* **2,** 429 (1935).
(10) Lilley, J. C., Legallais, Victor, Cherry, Ruth, *J. App. Phys.* **18,** 613, 1947.
(11) Philipp, H. J., *J. Polymer Sci.* **6,** 371 (1951).
(12) Rolfson, F. B., ANAL. CHEM. **35,** 1303 (1963).
(13) Seeley, S. W., Anderson, E. I., *RCA Review* **5,** 77 (1940).
(14) Staverman, A. J., *Rec. Trav. Chim.* **70,** 344 (1951); *Ibid.*, **71,** 623 (1952).
(15) Staverman, A. J., *et al.*, *J. Polymer Sci.* **23,** 57 (1957).
(16) Stockmayer, W. H., Casassa, E. F., *J. Chem. Phys.* **20,** 1560 (1952).

RECEIVED for review June 17, 1963. Accepted January 13, 1964.